



## Syntheses and characterization of iridium and rhodium ethylene complexes containing a doubly linked cyclopentadienyl ligand

Robert M. Chin<sup>a,\*</sup>, Devin Maurer<sup>a</sup>, Mitchell Parr<sup>a</sup>, Neysa Allworth<sup>a</sup>, Robbie Schwenker<sup>a</sup>, Daniel Sullivan<sup>a</sup>, Samantha Enabnit<sup>a</sup>, William Brennessel<sup>b</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423, United States

<sup>b</sup> Department of Chemistry, University of Rochester, Rochester, NY 14627, United States

### ARTICLE INFO

#### Article history:

Received 12 April 2008

Received in revised form 15 April 2008

Accepted 15 April 2008

Available online 22 April 2008

#### Keywords:

Iridium

Rhodium

Cyclopentadienyl

Dinuclear

Fulvene

### ABSTRACT

The dimerization of 6,6-dimethylfulvene with Ni(cod)<sub>2</sub> yields the 4,4,8,8-tetramethyl-3a,4,7a,8-tetrahydro-*s*-indacene isomer (**1a**). Heating a solution of **1a** converts it to the 1,4,5,8 (**1b**) and 1,4,7,8 (**1c**) tetrahydro-*s*-indacene isomers. The activation energy for the isomerization is 23(1) kcal/mol. **1b** and **1c** can be deprotonated with *n*-BuLi and the reaction of the dianion with [ClIr(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> gives two isomers, *cis*-[(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)(CMe<sub>2</sub>)Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> (*cis*-**2**) and *trans*-[(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)(CMe<sub>2</sub>)Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> (*trans*-**2**). Reaction of **1b** and **1c** with RhCl<sub>3</sub> · xH<sub>2</sub>O in refluxing methanol yields a red-orange solid, which was consistent with the empirical formula, [(C<sub>5</sub>H<sub>3</sub>)(CMe<sub>2</sub>)RhCl<sub>2</sub>]<sub>n</sub> (**3**). Reaction of **3** with C<sub>2</sub>H<sub>4</sub> in a Na<sub>2</sub>CO<sub>3</sub>/ethanol mixture afforded *cis*-[(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>)(CMe<sub>2</sub>)Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> in 5% yield.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Linked cyclopentadienyl ligands have been previously synthesized to study the interaction of two metal centers next to each other. The dicyclopentadienyl ligands typically have one or two linking units. For the singly linked ligands, the bridging groups can vary from methylene [1], dimethylsilylene [2], dimethylmethylene [3] to no intermediate group as in fulvalene (Scheme 1) [4].

One of the problems with the singly linked ligands is that the two metal centers are not always next to each other due to the free rotation about the linking unit. Use of two linkers would stop the free rotation of the cyclopentadienyl rings and ensure that the two metal centers stay close to one another (Scheme 2).

While there have been a number of complexes reported containing different linking groups [3], one combination that is conspicuously absent is the one containing two CMe<sub>2</sub> groups as the linkers. In 1979, McGlinchey and coworkers reported the synthesis of two isomers of 4,4,8,8-tetramethyl-tetrahydro-*s*-indacene, the 1,4,5,8 (**1b**) and 1,4,7,8 (**1c**) isomers. The products were formed via the dimerization of 6,6-dimethylfulvene using nickel atoms in a metal atom reactor [5]. The expected 3a,4,7a,8 isomer, **1a**, was never isolated but was presumed to be the common intermediate in the formation of **1b** and **1c** (Scheme 3).

Herein we report the solution syntheses and characterization of **1a**, **1b**, and **1c** from commercially available reagents, and the subsequent syntheses and characterization of three iridium and rhodium ethylene complexes containing this robust and versatile ligand with two CMe<sub>2</sub> linkers.

### 2. Experimental

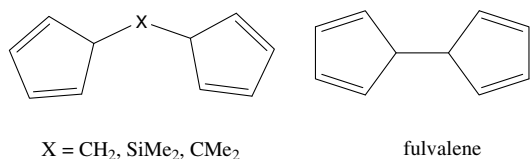
#### 2.1. General procedures

Reactions that required inert conditions were performed using modified Schlenk techniques or in an MBraun Unilab glovebox under a nitrogen atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Unity Inova 400 MHz or GE-QE 300 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are given relative to the residual proton or <sup>13</sup>C solvent resonances. Mass spectra were recorded on a Hewlett–Packard 6890-5973 GC–MS. X-ray data were collected on a Bruker SMART Apex II CCD Platform diffractometer.

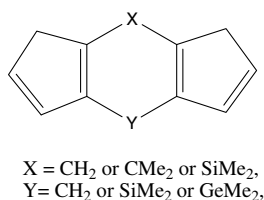
#### 2.2. Solvents and reagents

Unless otherwise indicated, all chemicals were used as received (reagents from Aldrich, Acros, or Strem Chemical Company). Deuterated solvents were obtained from Cambridge Isotope Laboratories. Tetrahydrofuran (THF), benzene, dichloromethane, and pentane were passed through an MBraun Solvent Purification

\* Corresponding author. Tel.: +1 319 273 7898; fax: +1 319 273 7127.  
E-mail address: martin.chin@uni.edu (R.M. Chin).



**Scheme 1.** Examples of singly linked Cp ligands.



**Scheme 2.** Examples of doubly linked Cp ligands.

System prior to use. C<sub>6</sub>D<sub>6</sub> was distilled from a dark purple solution of sodium benzophenone ketyl. CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> were distilled under vacuum from CaH<sub>2</sub>. Elemental analyses were either performed by Atlantic Microlab, Norcross GA, or on a Thermo Flash EA1112 Series analyzer at the National Ag-Based Industrial Lubricant laboratory in Waverly, IA. 6,6-dimethylfulvene was obtained from Aldrich or prepared as described [6]. Ni(cod)<sub>2</sub> was purchased from Strem Chemical or prepared as described [7]. [IrCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> was prepared according to the literature method [8]. 4,4,8,8-Tetramethyl-1,4,5,8-tetrahydro-*s*-indacene, **1b**, and 4,4,8,8-tetramethyl-1,4,7,8-*s*-indacene, **1c** were prepared as described [5] or by using Ni(cod)<sub>2</sub> as a reactive source of nickel. Cl<sub>2</sub> gas was prepared by the reaction of 6 M HCl with household bleach (5% NaOCl) as described by Mattson and coworkers [9].

### 2.2.1. Preparation of **1a** using Ni(cod)<sub>2</sub> as a reactive source of nickel

6,6-Dimethylfulvene (6.6383 g, 62.6 mmol) was placed in a 100 mL cylindrical drying chamber and stirred vigorously in a nitrogen filled glove box. Ni(cod)<sub>2</sub> (6.5823 g, 23.93 mmol) was added all at once to the stirred 6,6-dimethylfulvene. The mixture darkened immediately and became highly viscous. Approximately 8 mL of C<sub>6</sub>H<sub>6</sub> was then added to the reaction and stirred manually with a spatula for 10 min. Unreacted 6,6-dimethylfulvene and benzene were removed under vacuum inside the glove box. The resulting black residue was suspended in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> and added to ~100 mL of stirred hexane inside a 250 mL Erlenmeyer flask. The

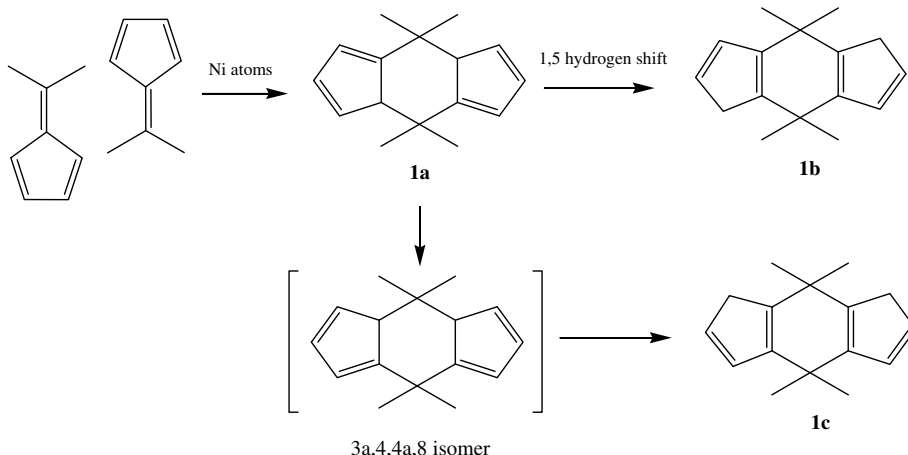
mixture was then filtered through a SiO<sub>2</sub> padded frit and the filtrate collected. The hexane was removed by rotary evaporation resulting in an oil to which was added ~25 mL of methanol. The methanol/oil mixture was placed into an ice bath forming a white crystalline precipitate. The mixture was filtered and washed with cold methanol to give **1a** as a white solid (0.520 g, 8% yield). *Safety note: The black nickel residue on the SiO<sub>2</sub> padded frit would sometimes smoke upon standing in the hood. We now pour dilute aqueous (~1 M) HCl onto the black Ni residue and then cover the mixture to deactivate any reactive Ni metal.* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 21 °C), δ 6.39 (m, 2H), 6.25 (m, 2H), 6.12 (m, 2H), 2.96 (m, 2H), 1.49 (s, 6H), 0.75 (s, 6H) <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub> 20 °C) δ 159.92 (quat C), 132.65, 132.26, 121.67 (CH), 61.76 (CH), 38.39 (C(CH<sub>3</sub>)<sub>2</sub>), 27.07 (CH<sub>3</sub>), 25.00 (CH<sub>3</sub>). Anal. Calc. for C<sub>16</sub>H<sub>20</sub>: C, 90.60; H, 9.40. Found: C, 90.62; H, 9.46%. MS (EI, 70 eV, *m/z*) 212 (17), 197 (100), 183 (82), 167 (25), 165 (27), 152 (15).

Alternatively, **1b** and **1c** can be prepared by heating **1a** in situ. The synthesis was carried out as described above except instead of adding MeOH to precipitate **1a**, the resulting oil was heated at 80 °C for 30 min, at which point the oil became a semi-solid. The resulting solid was sublimed at 80 °C, 20 mtorr, to give a white solid mixture of **1a** and **1b** (20% yield). The <sup>1</sup>H NMR spectral data matched the reported data in CD<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 21 °C), δ 6.55 (m, 2H), 6.36 (dt, *J* = 5.3, 1.4 Hz, 2H), 3.03 (m, 4H), 1.34 (s, 3H), 1.32 (s, 6H), 1.31 (s, 3H).

The kinetic data for the isomerization of **1a** to **1b** and **1c** were collected as follows:

One mL (0.026–0.071 M) CDCl<sub>3</sub> solutions of **1a** were charged into a J. Young NMR tube and 5 μL of toluene added via microsyringe. The tube was kept in an ice bath upon mixing and transferred quickly into the NMR spectrometer. The temperature of the NMR probe was maintained using a Varian variable temperature controller and the temperature was calibrated using ethylene glycol and standard operating procedures. Approximately 10–20 spectra were obtained at regular time intervals over the period of 2–3 half lives for each sample of a given temperature. The NMR spectroscopic data was integrated using ACDLABS version 10.0.2 1D NMR Processor software. The resulting data was then analyzed by Microsoft Excel.

*Preparation of cis-2 and trans-2.* A mixture of **1b** and **1c** (470.5 mg, 2.22 mmol) was placed in a 100 mL flask and 12 mL of THF added. *n*-BuLi (1.8 mL, 2.5 M solution in hexanes) was added dropwise to the stirred solution at 21 °C. A white participate formed towards the end of the *n*-BuLi addition. The mixture was stirred for 20 min and the THF was then removed in vacuo. The resulting dianion was re-suspended in 10 mL of pentane.



**Scheme 3.** Proposed mechanism for the formation of **1b** and **1c** by McGlinchey and coworkers.

Download English Version:

<https://daneshyari.com/en/article/1307144>

Download Persian Version:

<https://daneshyari.com/article/1307144>

[Daneshyari.com](https://daneshyari.com)